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OFFICE OF NAVAL RESEARCH

FINAL REPORT.

1 July 1979 — 30 November 1980

ELECTROCHEMISTRY AT VERY SMALL ELECTRODES

Contract N00014-79-C-0644

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A theory has been developed which describes the diffusion-limited current flowing at a finite disk electrode embedded in an infinite insulating plane. The theory has been confirmed experimentally using electrode arrays prepared from glassy carbon substrates overlaid by insulating resist material.

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Final Technical Report

During the period of this contract Dr. Koichi Aoki was employed for the period July 1979-August 1980 and Dr. Tadeusz Hepel and Dr. Maria Hepel were employed for the period September-November 1980.

The work of Dr. Aoki resulted in two technical reports (N00014-79-C-0644, No.'s 1 and 2) and two manuscripts submitted for publication. One has been published (Koichi Aoki and Janet Osteryoung, J. Electroanal. Chem. 122 (1981) 19-35. Diffusion-controlled current at the stationary finite disk electrode. Theory). The second is in press (Koichi Aoki and Janet Osteryoung, J. Electroanal. Chem., in press; Diffusion-controlled current at a stationary finite electrode. Experiment).

The substance of this work is as follows. Although many publications exist on the subject of chronoamperometric currents at finite disk electrodes all previous theories were incorrect for they ignored the effect of edge effects on the concentration profiles at the electrode as a function of time. The present solution is exact and is expressed as a combination of an asymptotic series and descending series of the dimensionless parameter $\underline{\tau} = 4\underline{D}t/\underline{a}^2$ where $\underline{D}$ is the diffusion coefficient of the reactant, $\underline{t}$ the time, and $\underline{a}$ the electrode radius. The asymptotic series describes the current for small values of τ while the descending series describes the current for large values of $\underline{\tau}$. The two series have essentially the same values over the range $1 < \tau < 4$, and the asymptotic series approaches the Cottrell equation as $\underline{\tau}$ approaches zero while the descending series approaches the well-known steady-state current as $\underline{\tau}$ approaches infinity. The availability of this exact solution, valid

over all values of $\underline{\tau}$, makes it possible for the first time to characterize electrode geometry by electrochemical techniques and to do absolute experiments which provide values of $\underline{D}$. It should be noted in passing that the independent determination of $\underline{D}$ has been an important and difficult experimental problem.

The second paper confirms experimentally the theory discussed above. The experimental problem was to design and construct electrodes of known geometry so that the geometry of a conducting disk embedded in an infinite insulating plane, the model for the theory, would be duplicated faithfully in the experiment. A second objective was to produce electrodes of accurately known radius, so that the dependence of current on electrode radius could be tested explicitly. These ends were met by constructing electrodes of glassy carbon (3 mm in diameter) overlaid by an insulating mask. The mask was prepared using electron-beam lithography. Electrode diameters in the range 20-200 μm were chosen to cover the desired range of τ at convenient measurement times (0.05-3 s). The predictions of the theory were confirmed over the entire range of $\underline{a}$ and $\underline{t}$ investigated (ie - 0.003-20). This detailed experimental confirmation now makes it possible to use the theory to investigate the geometry of small electrodes or of other conducting structures which can be examined electrochemically.

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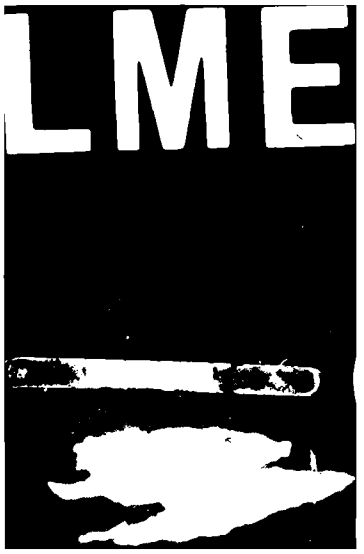
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